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**FLUORIC ANIONIC CONDUCTORS IN THIN LAYERS,
THEIR MANUFACTURE AND THEIR ELECTROCHEMICAL APPLICATIONS**
[Conducteurs anioniques fluorés en couches minces,
leur fabrication et leurs applications électrochimiques]

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The present invention concerns novel structures for fluoric

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anionic conductors according to the principal patent application No. 75/33244, their manufacture and their electrochemical applications.

Described in the principal application are conductors constituted by solid solutions of at least two fluorides that form lacunar fluorides.

The lacunae of these solid solutions result from the substitution, in the first fluoride, of at least one other fluoride possessing a cation with a valence different from that of the first, this substitution being effected between the fluorides in question within the limits of the possible solid solutions.

The augmentation of the number of lacunae in the secondary anionic network of the first fluoride makes it possible to obtain an even higher conductivity. This latter is improved still further, if the fluorides employed possess cations that can be strongly polarized.

The choice of the cation utilized for the substitution is in general imposed by its magnitude, which must be close to that of the ion that it will replace, so that the structure of the reference fluoride will be preserved.

The corresponding conductors possess, starting from ambient temperature, an elevated conductivity via fluoride ions, which thus confers performances of great interest upon those devices containing them and, in an advantageous manner, present melting temperatures clearly lower than those of the ionic conductors more currently employed, such as β alumina.

The field of application and technical advantages of these conductors are found at present to be considerably increased by virtue of the possibility, established by the invention, of producing structures according to a new structure.

The inventors have in fact determined that those conductors referenced above can be

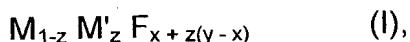
produced in the form of thin layers and that, in a remarkable manner, while perceptibly retaining the same properties as in the massive state.

The production of the conductors in question in the form of thin layers is of interest to the extent that it permits taking advantage of their elevated performance in the field of microelectronics.

The invention thus seeks to provide new structures in the form /2 of thin layers produced from anionically conductive materials according to the principal patent application and new high-performance devices comprising such structures.

The structures according to the invention are constituted by solid solutions in the form of thin layers with at least two fluorides that form lacunar fluorides. The cations of these fluorides, one of which possesses a valence different from that of the others, are chosen in such a way that the conductivity of the resulting conductor will be adequate at the temperatures of application. It will be noted in this regard that it is generally admitted that conductivity is industrially exploitable when it is above about $10^{-7} \Omega^{-1} \text{cm}^{-1}$ at the temperature at which it is desired to work.

According to one embodiment mode of the invention, the lacunar fluorides in thin layers, formed from two fluorides MF_x and $M'F_y$, answer to general formula I:



in which

M and M' represent, respectively, a cation capable of forming lacunar fluorides with sufficient conductivity at the temperatures of application, the valences x and y of these cations being different,

z is a number chosen in a domain that is a function of the pair of cations M and M', whose limits are imposed by the limits of the solid solutions possible between MF_x and $M'F_y$.

A preferred group of lacunar solid solutions of this type is formed from the fluorides MF_2 and $M'F_3$, and answers to formula II:



In this formula, z is advantageously comprised between 0 and 0.5 and preferably 0.20 and 0.30, and M and M' are, respectively, divalent or trivalent cations.

The compounds in this group comprise lacunar fluorides in which M and M' are respectively Pb and Bi.

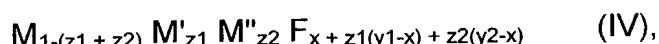
Another preferred group of solid solutions is formed from the fluorides MF and $M'F_3$ and presents formula III:



in which M is a monovalent cation, M' is a trivalent cation, and z is a number from 0.50 to 0.75.

M is advantageously selected in the group comprising Ag, Au, Ti, Rb, K, and M' in that group comprising Bi, As or Sb.

According to another embodiment mode of the invention, the lacunar fluorides in thin layers, which result from three fluorides MF_x , $M'F_{y1}$ and $M''F_{y2}$, answer to general formula IV:



in which

- M, M' and M'' each represent a cation capable of forming lacunar fluorides with sufficient conductivity at the temperatures of application,

- x, y₁ and y₂ represent the valences of cations, at least one of these valences being different from the others,
- z₁ and z₂ are two numbers chosen in a domain that is a function of the group of cations M, M' and M'', and whose limits are imposed by the limits of the possible solid solutions between MF_x, M'F_{y₁} and M''F_{y₂}.

In another embodiment mode of the invention, the cations of the lacunar fluorides in thin layers are chosen, under the reservation of the above-indicated criteria, in that group constituted by Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Ag⁺, Ti⁺, NH₄⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Cd²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Sn²⁺, Al³⁺, Ga³⁺, In³⁺, Sc³⁺, Y³⁺, lanthanides (from La³⁺ to Lu³⁺), Sb³⁺, Bi³⁺, Ti⁴⁺, Zr⁴⁺, Hf⁴⁺, Te⁴⁺, I⁵⁺ and, preferably, in the group constituted by K⁺, Rb⁺, Cs⁺, Ag⁺, Ti⁺, NH₄⁺, Sr²⁺, Ba²⁺, Cd²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Sn²⁺, La³⁺, Sb³⁺, Bi³⁺, Te⁴⁺, I⁵⁺.

The production of the fluoric anionic conductors in thin layers according to the invention is carried out advantageously according to the techniques of thin-layer deposition.

It is thus possible to proceed to a thermal evaporation, under vacuum, of fluorides with respective cations that answer to those characteristics indicated above. It is then possible to operate either by evaporation of the compound from a single crucible, or to proceed via co-evaporation of simple fluorides, which is preferable.

In this latter case, the starting fluorides, applied in those proportions respectively permitting the formation of the desired lacunar solid solutions, are each placed in crucibles arranged in an enclosed space in which a high vacuum has been created.

The co-evaporation is produced by heating each of the crucibles to temperatures suitable for that purpose. The fluoride vapors formed precipitate onto an insulating substrate

positioned in their path. For certain compounds, it can be useful to heat the substrate. The rate of deposition shall be chosen in a manner that assures optimal properties to the thin layer produced; it will depend upon the nature of the compound deposited.

Numerous other techniques can be utilized to prepare the deposits of lacunar fluorides. Let us cite flash evaporation, electronic bombardment, cathode or ionic sputtering, chemical methods, etc. A description of these methods can be found for example in the *Handbook of Thin-Film Technology* by L. I. Moussel and R. Glang, published by the McGraw Hill Book Company.

Variants or adaptations of these methods, or other known methods for the deposition of thin layers in general, will be easily applied by the man of art to obtain lacunar solid solutions in thin layers according to the invention.

Nevertheless, those methods permitting separate control of the condensation rates for each simple fluoride occurring in the solid solution are necessary to obtain composition gradients such as those described below.

The studies carried out on these conductive solid solutions in thin layers show that they possess an ionic conductivity of the same order of magnitude as that observed in dense materials and function in a satisfactory manner, starting from room temperature, differing in that respect from those oxides ordinarily utilized, such as β alumina.

The aggregate of their properties, associated with their structure in thin layers, makes them valuable in numerous applications in which there is a desire to have an efficient source of energy available, which is miniaturized or integrated, or even for the manufacture of nonvolatile memories.

In particular, they have proven to be particularly suitable for the production of solid electrolytes in galvanic elements in thin layers, whether rechargeable or not.

The invention therefore aims likewise at those galvanic elements possessing a cathode and an anode in thin layers and comprising, as electrolytes, those fluoric anionic conductors in thin layers mentioned above.

By virtue of their minimal bulk, their total thickness being possibly as little as 1.3μ , these elements lend themselves conveniently to numerous applications in the field of microelectronics.

Their interest is further enhanced by the fact of the high performance of the electrolytes that they contain, which is found, in a remarkable manner, to be of the same order of magnitude as that in the solid state.

The galvanic elements are thus arranged in thin layers providing, in particular, EMFs that can reach about 1.5 V, capacitances of as much as $1 \text{ mA}_h/\text{cm}^2$ and current densities as high as $90 \mu\text{A}/\text{cm}^2$.

It will be noted, moreover, that satisfactory operation is obtained starting at ambient temperature.

According to the nature of the cations of the galvanic chain, it is also possible to produce rechargeable elements.

In the galvanic cells according to the invention, the electrolytes in thin layers comprise, advantageously, elements whose corresponding fluoric compounds are good ionic conductors.

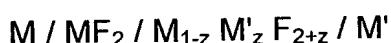
It is more particularly advantageous to employ electrodes, in particular, a cathode containing at least one of the cations present in the electrolyte.

A corresponding galvanic element, possessing a solid electrolyte in a thin layer with the formula $M_{1-z} M'^z F_{2+z}$, such as that indicated above, and an anode and a cathode respectively constituted by M and M', whose cations are respectively divalent and trivalent, will be formed in the initial state by the chain:



During normal discharge, the F^- ions, transported by the electrolyte, migrate toward the anode and form, with the cationic element of the same, the corresponding fluoric compound, and inversely during charging in the case of rechargeable cells.

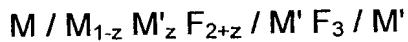
The corresponding chain during discharging, and possibly during charging, will therefore be the following;



According to the arrangement of the invention, the cathode of the galvanic elements of the invention comprises a thin layer of a metal whose corresponding cation is found in the electrolyte, this layer being covered from the side of the electrolyte, with a thin layer containing the fluoride of this cation.

This arrangement presents the advantage of providing galvanic cells that are spontaneously charged starting from the end of their manufacture and, in that case in which the cells will then be rechargeable, of avoiding an electrolysis that is too intense during their recharging operation.

A corresponding galvanic element, comprising the electrolyte with formula II above and respectively M and M' in the anode and the cathode, will then be constituted by the following chain in the initial state:



and during discharging, and when charging is needed:



According to another provision of the invention, for improving the performance of these galvanic elements in the form of thin layers still further, and for example to reduce the internal resistance resulting from interface phenomena between the solid electrolyte and the electrodes, recourse is had to elements comprising an electrolyte formed from solid solutions of lacunar fluorides, whose composition varies gradually, on the one hand, toward the anode and/or, on the other, toward the cathode, and this in such a way that the fluoride or fluorides in it or them, which contain the same cation or cations as those present in the anode, will be progressively enriched, and inversely from the side of the cathode.

The corresponding galvanic chain of an element comprising M and M', respectively at the anode and at the cathode, and the electrolyte taken as an example above, will be the following at the initial moment:



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with $a > z$ and tending progressively toward 1, and $b < z$ and tending progressively toward 0.

According to a supplementary provision, to reduce the discontinuities at the electrode - electrolyte interfaces still further, and to effect a continuous reduction of the internal resistance as a result, the structures and thin layers of the anode and/or of the cathode are such that their composition will vary progressively toward the electrolyte so as to become gradually enriched in the composition of the corresponding fluorides present in the electrolyte.

It is likewise possible to produce structures in the form of thin layers for the anode and/or the cathode, comprising, in the dispersed state, a derivative that leads to fluorides

during charging or discharging.

To produce the galvanic elements of the invention, the initial step is to produce successive deposits on each of those compositions constituting the electrochemical chain by utilizing the classical techniques for the deposition of thin layers, such as those listed above.

By for example employing the technique of evaporation under vacuum, the electrode formed by elements having the highest evaporation temperature is deposited under vacuum on an insulating substrate, for example, mica, which is followed by the co-evaporation of those fluorides permitting the formation of the desired lacunar solid solution and, finally, the evaporation of that compound destined to form the second electrode.

When the intention is to form composition gradients according to the provisions of the invention described above, the co-evaporation steps are carried out in such a way that the deposition rate of one of the compounds is progressively reduced to 0.

The primary or secondary galvanic elements in the form of thin layers, thus constituted, possess transport properties of great interest.

These properties can be exploited in an advantageous manner starting already from ambient temperature, and in a temperature zone corresponding to those in which the work is ordinarily carried out and ranging up to about 400°C.

Conspicuous, moreover, is the remarkable stability of the invented structures in the form of thin layers with regard to atmospheric agents and the temperature, which increases their interest still further.

These elements have proven to be advantageously utilizable in a large number of

industrial applications in the field of microelectronics.

They can for example be utilized in the manufacture of electric watches and of microcalculators or even in biotelemetry.

Other characteristics and advantages of the invention will become apparent in the following examples and by turn to the drawings to which reference is made.

EXAMPLE 1:

The production of thin layers of a compound with the formula:

$Pb_{1-z} Bi_z F_{2+z}$, in which $z = 0.25$.

This compound is obtained by thermal co-evaporation of the fluorides PbF_2 and BiF_3 under vacuum.

The fluorides in question are respectively placed in crucibles arranged in an enclosed space where a high vacuum in the order of 10^{-6} torr is created. The quantities employed correspond respectively to a molar ratio of 1 to 3.

The crucibles, connected to independent heating controls, are heated to temperatures suitable for inducing the simultaneous evaporation of the fluorides.

These fluoride vapors are deposited on a mica substrate left at ambient temperature.

The deposition is regulated to a rate of 10 Å/s.

The thickness of those layers of lacunar fluorides formed is monitored by measuring the oscillation frequency of a quartz (previously calibrated) placed near the substrate onto which the fluorides in question are being deposited at the same time.

The obtained compound consisting of thin layers is characterized according to the methods of classical analysis, such as the diffraction of X-rays or nuclear microanalysis (retrodifusion of α particles). It is verified that it is a matter of a solid solution of lacunar

fluorides of the fluorite type. The impurity levels are very low (< 0.1%).

The conductivity of the material in thin layers, measured according to conventional techniques employing alternating current with a variable frequency is in the order of from $10^{-2} \Omega^{-1} \text{ cm}^{-1}$ to

$10^{-3} \Omega^{-1} \text{ cm}^{-1}$ at 200°C , which corresponds practically to that observed with the dense material.

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Produced, by proceeding according to a comparable mode of operation, are thin layers of compounds answering to the formula $M \text{ bi } F_4$, in which M represents a monovalent cation constituted by thallium, rubidium or potassium.

The lacunar fluorides obtained in the form of thin layers are of the fluorite type.

The study of their transport properties shows that they possess conductivity of the same order of magnitude as those of fluorides in the corresponding dense state.

The curves representing the logarithmic variation of the conductivity, $\log \sigma$ (in $\Omega^{-1} \text{ cm}^{-1}$) as a function of $10^{-3} T^{-1} (\text{K}^{-1})$, are reported in Fig. 1.

EXAMPLE 2:

The production of a galvanic element in the form of thin layers comprising the chain:



in which z is a number from 0.1 to 0.5.

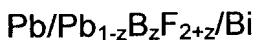
The deposition of the various layers of those compounds constituting the galvanic element takes place by the use of a technique employing evaporation under vacuum, such as that in Example 1. Formed, therefore, is a structure of the sandwich type, with superimposed layers.

Carried out first of all, according to the geometry desired, is the deposition of a layer of

Bi at the rate of 40 Å/s, then of a solid solution of lacunar fluorides by utilizing PbF_2 and BiF_3 , according to those proportions respectively corresponding to the desired solid solution, at a rate of 40 Å/s, followed by the deposition of lead at the approximate rate of from 10 to 20 Å/s.

EXAMPLE 3:

The production of a galvanic element in thin layers comprising the chain:



in which z differs from zero on the side of the electrode made of lead to 1 on the side of the electrode produced from bismuth.

The cathode, the electrolyte and then the anode are produced by proceeding successively with the deposition of layers of Bi, BiF_3 , then BiF_3 , PbF_2 and, finally, PbF_2 , Pb.

The procedure is the same as in Example 2, but the deposition is carried out at the rate of 40 Å/s, that of BiF_3 at from 2 to 3 Å/s,

and the deposition of the electrolyte layer is obtained, by the

co-evaporation at the rate of from 10 to 15 Å/s, of PbF_2 , BiF_3 and by causing the proportion of BiF_3 evaporating to decrease in such a way that the proportion of BiF_3 in the solid solution will diminish from the bismuth electrode toward the other electrode.

The anode, manufactured last of all, is produced by the co-evaporation of Pb_2 and Pb at the rate of from 10 to 20 Å/s, the deposition rate for PbF_2 tending progressively towards 0.

The element obtained will procure an EMF of 320 mV, which corresponds to the theoretical value deduced from the free energy of formation calculated from the thermodynamic data.

Seen in Figure 2 is the variation obtained with a unitary 0.1 cm² element consisting of thin layers, such as that described above, of the voltage at the boundaries (flow in a resistance

of 100 k Ω) as a function of the rate of discharge at ambient temperature (curve a).

Examination of this curve shows that it reaches a plateau after more than 4 hours of discharge, which corresponds to an average current density of 27 μ A/cm².

Entered on the same graph is the variation of the internal resistance as a function of the discharge time (curve b). It can be ascertained by referring to curve b that the invented galvanic element consisting of thin layers possesses a very low internal resistance. That is in fact only 8 k Ω at the beginning of discharge and does not reach more than 25 k Ω at the end of 4 hours of discharge.

Moreover, the specific energy deduced from these curves is in order of 0.05 Wh/g, which constitutes a noteworthy characteristic and is superior to that of the majority of thin-layer galvanic elements known up until now.

By proceeding as above, the following galvanic elements are produced, for which, respectively, the obtained EMF and capacitances are indicated. As for the electrolyte, the nature of the simple fluorides utilized to form the lacunar solutions is indicated.

<u>galvanic chain</u>	<u>EMF in V</u>	<u>Capacitances in Wh/g</u>
Co/CoF ₃ , PbF ₂ /Pb	0.75	0.304
Pb/PbF ₂ , AgF/Ag	1.29	0.150
Au/AuF ₃ , PbF ₂ /Pb	1.95	0.278

Likewise reported are the EMFs obtained with galvanic in the form of thin layers, produced according to the above-indicated technique of co-evaporation under vacuum, of the type:

<u>galvanic chain</u>	<u>EMF in V</u>
Pb/PbBiF ₄ /Bi	0.33
Ag/AgBiF ₄ /Bi	0.96

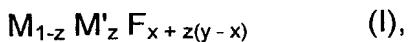
The results as a group show performance of great interest on the part of the elements according to the invention.

These unitary elements can be assembled in such a way that a large active surface is produced. It is possible to utilize several elements in the form of thin layers, such as those described above, and to superimpose them in order to form successive layers possessing a common electrode.

It is likewise possible to form layers with a large surface by depositing unitary elements on a "rolled" flexible support according to the technique utilized for capacitors.

1. Fluoric anionic conductors in the form of thin layers constituted by solid solutions of at least two fluorides that form lacunar fluorides, the cations of these fluorides, at least one of which possesses a valence different from that of the others, being chosen in such a way that the conductivity of the resulting conductor will be sufficient at the temperatures at which it will be used.

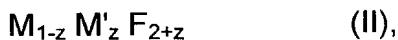
2. Fluoric anionic conductors in the form of thin layers, resulting from two fluorides, MF_x and $M'F_y$, answering to general formula I:



in which

- M and M' represent, respectively, a cation capable of forming lacunar fluorides with sufficient conductivity at the temperatures of application, the valences x and y of these cations being different,
- z is a number chosen in a domain that is a function of the pair of cations M and M' , whose limits are imposed by the limits of the solid solutions possible between MF_x and $M'F_y$.

3. Fluoric anionic conductors in the form of thin layers according to Claim 2, formed from the fluorides MF_2 and $M'F_3$, and answers to formula II:



in which z is advantageously comprised between 0 and 0.5 and preferably 0.20 and 0.30.

4. Fluoric anionic conductors in the form of thin layers with formula:



in which z is comprised between 0 and 0.5 and is preferably in the order of 0.25.

5. Fluoric anionic conductors in the form of thin layers according to Claim 2, formed from the fluorides MF and $M'F_3$ and presents formula III:



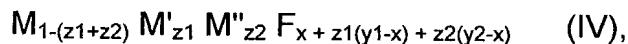
in which M is a monovalent cation, M' is a trivalent cation, z being a number from 0.50 to 0.75.

6. Fluoric anionic conductors in the form of thin layers

according to Claim 5, in which M is chosen in the group comprising

Ag, Au, Tl, K and Tb and M' in the group containing Bi, As and Sb.

7. Fluoric anionic conductors in the form of thin layers according to Claim 5, resulting from three fluorides MF_x , $M'F_{y1}$ and $M''F_{y2}$, and answering to general formula IV:



in which

- M , M' and M'' each represent a cation capable of forming lacunar fluorides with sufficient conductivity at the temperatures of application,
- x , y_1 and y_2 represent the valences of cations, at least one of these valences being different from the others,
- z_1 and z_2 are two numbers chosen in a domain that is a function of the group of cations M , M' and M'' , and whose limits are imposed by the limits of the possible solid solutions between MF_x , $M'F_{y1}$ and $M''F_{y2}$.

8. Fluoric anionic conductors in the form of thin layers according to any one of the Claims 1 to 3, 5 and 7, in which the cations of the corresponding component fluorides are chosen in the group constituted by Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Ag^+ , Tl^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Sn^{2+} , Al^{3+} , Ga^{3+} , In^{3+} , Sc^{3+} , Y^{3+} , Ianthanides (from La^{3+} to Lu^{3+}), Sb^{3+} , Bi^{3+} , Ti^{4+} , Zr^{4+} , Hf^{4+} , Te^{4+} , I^{5+} and, preferably, in that group constituted by K^+ , Rb^+ , Cs^+ ,

Ag^+ , Ti^+ , NH_4^+ , Sr^{2+} , Ba^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Sn^{2+} , La^{3+} , Sb^{3+} , Bi^{3+} , Te^{4+} , I^{5+} .

9. Fluoric anionic conductors in the form of thin layers, chosen in the group comprising

$\text{Pb}_{1-z}\text{Co}_z\text{F}_{2+z}$, $\text{Pb}_{1-z}\text{Ag}_z\text{F}_{2+z}$,

$\text{Pb}_{1-z}\text{Au}_z\text{F}_{2+z}$.

10. Fluoric anionic conductors in the form of thin layers, chosen in the group comprising PbBiF_4 , AgBiF_4 and TiBiF_4 .

11. Process for the production of fluoric anionic conductors in the form of thin layers according to any of the Claims 1 to 10, characterized by the fact that it is carried out by the thermal evaporation, under vacuum, of simple fluorides respectively answering to those characteristics indicated above.

12 - Process according to Claim 11, characterized by the fact /14
that the simple fluorides, employed according to those respective proportions permitting the formation of the desired lacunar solid solutions, are submitted to co-evaporation and placed for this purpose in separate crucibles arranged in an enclosed space in which a high vacuum is created and heated to temperatures permitting said co-evaporation to be achieved, the fluoride vapors formed being deposited on an insulated substrate placed in their path.

13 - Application of the fluoric anionic conductors in the form of thin layers according to any one of the Claims 1 to 11 as electrolytes.

14 - Galvanic cells in which the various elements constituting the galvanic chain are formed into thin layers and comprise, as electrolyte, the fluoric anionic conductors in the form of thin layers according to any one of the Claims 1 to 10.

15 - Galvanic cells according to Claim 14, in which at least one of the electrodes contains an element in which the corresponding fluoric compound is a good ionic conductor.

16 - Galvanic cells according to any one of the Claims 14 or 15, in which the electrodes, particularly the cathode, contains at least one of those cations present in the electrolyte.

17 - Galvanic cells according to any one of the Claims 14 to 16, in which the cathode comprises a thin layer of a metal whose corresponding cation is present in the electrolyte, this layer being covered on the side of the electrolyte with a thin layer of the fluoride of this cation.

18 - Galvanic cells according to any one of the Claims 14 to 17, comprising an electrolyte in the form of thin layers formed by lacunar, fluoric solid solutions, whose composition varies gradually on the one hand toward the anode and/or, on the other, toward the cathode, and this in such a way that the fluoride or fluorides in it or them, which contain the same cation or cations as those present in the anode, will be progressively enriched, and inversely from the side of the cathode.

19 - Galvanic cells according to any one of the Claims 14 to 18, in which the composition of the anode and/or the cathode varies progressively toward the electrolyte in such a way that corresponding fluorides present in the electrolyte are gradually enriched therein.

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20 - Galvanic cell in the form of thin layers comprising, in the initial state, a chain of the type:

$M / M_{1-z} M'_z F_{2+z} / M'$

or

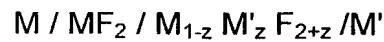
$M / M_{1-z} M'_z F_{2+z} / M'F / M'$

or

$M / M_{1-b} M'_b F_{2+z} / M_{1-z} M'_z F_{2+z} / M_{1-a} M'_a F_{2+a} / M' ,$

in which M and M' are elements constituting, respectively, the anode and the cathode, and respectively contain a divalent cation and a trivalent cation, z is comprised between 0 and 0.5, a is greater than z and tends progressively toward 1, and b is less than z and tends progressively toward 0,

and respectively, during discharge or if necessary during charging, a chain of the type:



or



or

